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No. Hei 4[1992]-95766

OXYGEN SENSOR MANUFACTURING METHOD

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OXYGEN SENSOR MANUFACTURING METHOD
[Sanso sensor no seizo hoho]

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Claims

/1*

1. An oxygen sensor manufacturing method, characterized by the fact that, in the oxygen sensor manufacturing method provided with a first process for the formation of an electrode on the solid electrolyte proper, and a he second process for the formation of a covering,

in the first process mentioned previously, a coated film consisting of an organic noble-metal ink containing an organic noble-metal compound is formed on the solid electrolyte proper mentioned previously, then with said coated film being baked to form a noble-metal-nuclei rendered formation part;

next, with a pleated layer being formed on the previously mentioned noble-metal-nuclei rendered formation part by the plating method, to form the previously mentioned electrode constituted by the previously mentioned noble-metal-nuclei rendered formation part and the previously mentioned plated layer formed on said formation part.

2. The oxygen sensor manufacturing method described in Claim 1, in which the noble-metal content in the organic noble-metal ink is 0.5-10 wt% with respect to the total amount of said organic noble-metal ink.

[Numbers in the margin indicate pagination in the foreign text.]

Detailed explanation of the invention

Industrial application field

The present invention relates to an oxygen sensor manufacturing method. More specifically, it relates to a method for the manufacture of an oxygen sensor that is excellent with regard to the adherence of the electrode onto the solid electrolyte proper as well as contamination resistance, insulation characteristics, productivity, economy, and a variety of characteristics accompanying this.

The present invention is utilized in a zirconia lambda [unconfirmed translation] sensor, an air-fuel ratio sensor, and so on in, for example, an internal combustion engine and a variety of other combustion machines.

Prior art

Since the ceramic oxygen sensor is capable of detecting the oxygen concentration over a wide range, has a fast response, as well as high-temperature resistance and other excellent characteristics, it is widely used in combustion machines, pollution measurements, etc.

For such an oxygen sensor, in general, a reference electrode, a measurement electrode, and other electrodes are formed in specified portions on the solid electrolyte proper. As the methods for the formation of these electrodes, ① a method in which a paste mainly consisting of Pt is coated on the unfired solid electrolyte proper and fired to form an electrode, and ② a /2 method in which electroless plating by a noble-metal salt or the

like is carried out with respect to the electrode formation predetermined portions on the solid electrolyte proper, are known (Japanese Kokoku Patent Nos. Sho 52[1977]-30699, Sho 59[1984]-24382, etc.).

Problems to be solved by the invention

However, in the conventional method described previously in ①, the sintering temperature for the ceramic proper is rate-controlling because the sintering of the ceramic proper and the electrode formation are carried out simultaneously by firing. As a result, excessive pores above the required porosity are formed in the electrode portions. The effect of the contamination substances in the atmosphere used is rendered during usage. Furthermore, for the electrodes formed by the conventional method described previously in ②, with the presence of a heating part on the ceramic proper surrounding these electrodes via an insulating layer, the insulating characteristics of the insulating layer portion may be damaged. Furthermore, a method for the formation of electrodes by the printing of an organoplatinum paste directly on the solid electrolyte proper can also be considered. However, in this method, it is difficult to obtain a platinum film that is sufficiently adhered. The reason is not clearly known. However, it is believed that, since the decomposition of the organic resin in the organoplatinum paste, detachment, and the sintering of platinum proceed simultaneously during the heating treatment, the sintering force functions above the adherence force with the solid electrolyte surface. To solve this, glass components and the like are added. However, in this method, the high catalytic activity required in the platinum film

may be damaged. Also, in the method for the formation of electrodes by the printing of an organoplatinum paste directly on this solid electrolyte proper, there is a problem with economics and so on because a large amount of platinum and the like is required. Moreover, in the case of printing on a curved surface, the operability is poor.

The present invention is to solve the problems mentioned previously. It provides a method for the manufacture of an oxygen sensor that is excellent with regard to the adherence of electrodes onto the solid electrolyte proper and in contamination resistance, insulating characteristics, productivity, and a variety of other characteristics accompanying this, due to the constitution of the electrode by the noble-metal-nuclei rendering formation part formed by an organic noble-metal ink (particularly with a 0.5-10 wt% noble-metal content) and the plated layer formed on top of this.

Means to solve the problems

The oxygen sensor manufacturing method related to the present invention is characterized by the fact that, in the oxygen sensor manufacturing method provided with a first process for the formation of an electrode on the solid electrolyte proper, as well as a second process for the formation of an electrode protective layer for the protection of said electrode by covering, in the first process mentioned previously, a coated film consisting of an organic noble-metal ink containing an organic noble-metal compound is formed on the solid electrolyte proper mentioned previously, then said coated film is baked to form a noble-metal-nuclei rendered formation part; next, a plated

layer is formed on the previously mentioned noble-metal-nuclei rendered formation part by the plating method.

As the "solid electrolyte proper" mentioned previously, those having a certain ionic conductivity are acceptable. For example, sintered bodies consisting of $\text{ZrO}_2\text{-Y}_2\text{O}_3$, $\text{ZrO}_2\text{-CaO}$, and other partially stabilized or stabilized types of zirconia and so on can be used. There are no special restrictions on the shapes as a whole. For example, there are cylindrical bodies having bottoms and flat plate-shaped bodies. Furthermore, there are no special restrictions on the thickness.

The "noble metal elements" in the "organic noble-metal compounds" mentioned previously are those having catalytic activity.

Specifically, Ag, Au, and platinum group elements (Ru, Os, Rh, Ir, Pd, and Pt) can be mentioned. It is possible to select, for use, an organic metal compound containing one or more noble metal elements, according to the objective and applications.

Furthermore, as shown in the present second invention, it is preferable that the noble metal content in the organic noble-metal ions is 0.5-10 wt% (to be simply called "%" hereafter) with respect to the total amount of the organic noble-metal ink. If it is less than 0.5%, since the nuclei formed will be too few, there is a practical problem in which the electroless reaction rate is too low during plating. On the other hand, if it exceeds 10%, the firing reaction of the noble metal will proceed simultaneously with the spalling of the organic resin during sintering and a sufficient film strength of the plated layer cannot be obtained.

The "baking" mentioned previously is for the formation of nuclei for activation on the solid electrolyte proper by an organic noble-metal ink containing the "organic noble-metal compound" mentioned previously, that is, noble metal nuclei.

Here, "nuclei" refers to the shaped bodies present in dots in mainly island shapes on the electrolyte proper. They function as a reduction reaction catalyst during the electroless plating reaction. There are no special restrictions on their sizes and shapes. In general, these nuclei are independent semispherical bodies of 0.1-0.8 μm . However, several of these may be piled. Furthermore, the baking temperature, heating time, and a variety of other conditions may be decided according to the types of the organic noble-metal ink, the solid electrolyte proper, the usage objectives of the oxygen sensor, etc. Furthermore, the formation of the coated film on the solid electrolyte proper of the organic noble-metal ink can be carried out by screen printing, transfer, etc. In particular, in the case of transfer, a coated film can be accurately formed onto the desired position on a curved surface. /3

The "noble-metal-nuclei rendered formation parts" mentioned previously refer to the portions (regions) in which the "nuclei" mentioned previously are gathered.

The "plated layer" mentioned previously is formed by deposition with mutually nonconnected noble metal nuclei as the center, followed by the connection of these noble metal nuclei. Therefore, it is made nonconductive by the formation of noble metal nuclei alone. With the formation of this plated layer, it will function as an electrode. Furthermore, it is unnecessary for this plated layer to be made of the same material as the noble-metal-nuclei rendered formation part. This may also be formed from other types of noble metals, as well as Ni and other metals. If these are made of the same type of material, the adherence is excellent. Furthermore, in the case of a noble metal material, the catalytic activity and the like are excellent.

Effects

In the present invention, first of all, the solid electrolyte proper or the like is coated with an organometal ink, then baked; noble metal nuclei in island shapes are strongly adhered and formed. Next, a plated layer is formed by the plating method in the region in which these noble metal nuclei are gathered, that is, on the noble-metal-nuclei rendered formation part. In this case, this plated layer can achieve a strongly bonded state with the solid electrolyte proper, with the noble-metal-nuclei rendered formation part acting as a go-between. Therefore, the electrode consisting of the noble-metal-nuclei rendered formation part and the plated layer formed on top of it is excellent in adherence with the solid electrolyte proper.

In the electrode portion formed in this manner, there is no concern about the formation of excessive pores. Furthermore, since the insulation characteristics of the insulation layer portion are not damaged, a sufficient performance as an oxygen sensor can be maintained.

Moreover, since the electrode is also free of discontinuity, baking several times is not required and the productivity is excellent. Furthermore, the reduction in the amount of usage of the high-cost organic noble metal is facilitated, making it excellent in terms of economics.

Moreover, during the formation of the plated layer, for example, in a plating liquid tank containing a noble metal compound, a noble-metal-nuclei rendered solid electrolyte proper or the like is introduced for electroless plating. In doing this, a plated layer is formed on this noble-metal-nuclei rendered formation part. Therefore, by the formation of the noble-metal-

nuclei rendered formation part in the desired shape, masking is not required during plating.

Application examples

With the application examples in the following, the present invention will be explained.

(1) Preparation of test specimens

① Application Product No. 1

As shown in Figure 1, on one surface (on the surface that is inside) of a $\text{ZrO}_2\text{-Y}_2\text{O}_3$ green sheet with a thickness of 0.3 mm, a Pt paste was coated by the printing method to form an inside electrode coated film (diameter 2.6 mm, length 6.5 mm, and thickness 15 μm) (2) and the inside lead drawing part (31) connected to this. Furthermore, the portion that is to be the outside electrode part (6) on the other surface (on the surface that is the outside) of this green sheet was removed. An alumina paste was coated by the printing method to form the first insulating layer coated film (8). Furthermore, at a location corresponding to the previously mentioned inside lead drawing part coated film (31), an outside lead drawing part coated film (32) was formed by the same method as said inside lead drawing part coated film on this first insulating layer coated film (8). Moreover, in the portions other than the open end portion (the portion to be connected to the outside electrode (6)) of the outside lead drawing part coated film (32) and the outside electrode formation prearranged part or the like, an alumina

paste was coated to form the second insulation layer coated film (9). Furthermore, in the portion that is to be the outside electrode (6), in order to render a stronger adherence force than the plated film, a zirconia paste obtained by the blending of particles (average granulated particle diameters 50-60 μm) consisting of the same material as the solid electrolyte used in the green sheet was coated. In this case, it is more preferable to use a material obtained at a blending ratio (the weight ratio) of the zirconia particles and the zirconia powder of 5:5 to 8:2 and at 1000-1350°C in relation to a material consisting of only zirconia particles with a few sintering contact points.

Separately, a circular cylindrical impedance tube (10) provided with holes (11a) and (11b) with a diameter of 1 mm at 180° opposite positions was prepared with the same material as the green sheet mentioned previously. Next, as shown in Figure 2, the coated-film-rendered green sheet was rolled on this impedance tube (9) so that the electrode (2) would cover the holes (11a) and (11b). By firing, the solid electrolyte proper (1A), the inside electrode (2A), the inside lead drawing part (31A), the outside lead drawing part (32A), the first insulation layer (8A), and the second insulation layer (9A) were obtained.

On the other hand, using a transfer printing pad (Tanbo printing machine) and with an organoplatinum ink (viscosity 80-200 poise, measured with a DV-II viscometer manufactured by the Brookfield Co.) consisting of an organoplatinum compound (with the platinum concentration being 2% in the organoplatinum ink) containing an organic binder, an ink pattern portion formed in a rectangular shape (2.5 mm x 6.5 mm x 0.1 mm) on a transfer plate was transferred to the external peripheral wall corresponding to the hole (11a) provided on the tube wall of the

solid electrolyte proper (1A) of the cylindrical body mentioned previously. A noble-metal-nuclei rendered formation part coated film (4) for use in the measuring electrode was formed. When the viscosity of this ink was 80-200 poise, the actual operability was good and it was good for transfer.

Furthermore, this was subjected to baking at 700°C for 2 h to form a noble-metal-nuclei rendered formation part (4A). These nuclei were semispherical bodies with a diameter and a height of about 0.3 μm . Since the resistance value of this noble-metal-nuclei rendered portion was infinitely large, it was found that the various nuclei were not connected.

Next, the impedance tube (10) having the noble-metal-nuclei rendered solid electrolyte proper was coated in an electroless plating liquid to form a plated layer (5) (please refer to Figure 3 and Figure 4) on the noble-metal-nuclei rendered formation part (4A). In doing this, an oxygen sensor element (Application Product No. 1) having an outside electrode (6) constituted by the noble-metal-nuclei rendered formation part (4A) and the plated layer (5) formed on top of it was prepared. This plating was carried out using a tetravalent Pt amine-complex salt aqueous solution, with hydrazine as a reducing agent, followed by deposition, drying, and a heat treatment (1000-1300°C, 1 h) in air.

② Application Product Nos. 2 through 4 and Comparative Product Nos. 1 through

Oxygen sensor elements were prepared in the same manner as Application Product No. 1 except that the platinum contents in the organoplatinum inks were 1, 5, and 10 wt%. These were

Application Products Nos. 2 through 4, respectively. Furthermore, in the same manner, oxygen sensor elements were prepared with platinum contents of 0.2, 15, 20, and 50 wt% in the organoplatinum inks to form Comparative Product Nos. 1 through 4, respectively.

③ Application Product Nos. 5 through 6

On the entire external peripheral surface of the oxygen sensor element of Application Product No. 1, spinel was further subjected to melt injection to form an electrode protective layer (7) of about $50\text{-}150\ \mu$, as shown in Figures 3 and 4. An oxygen sensor (Application Product No. 5) was prepared. Furthermore, an oxygen sensor (Application Product No. 6) having a structure with a heater (12) built into the alumina insulation layer of the oxygen sensor of Application Product No. 5 was prepared, as shown in Figure 5. This heater (12) was installed so that the electrode part was surrounded for the heating of the element (mainly the electrode part).

④ Simultaneously fired comparative product (No. 5)

In the same manner as the application products, on a $\text{ZrO}_2\text{-Y}_2\text{O}_3$ green sheet with a thickness of 0.3 mm, a Pt paste was coated by the printing method to form an inside electrode coated film and an inside lead drawing coated film connected with this. Furthermore, in the portions facing oppositely via a sheet in the inside electrode, using the same Pt paste, an outside electrode coated film and a lead drawing part coated film connected to this were formed by the same method. Furthermore, in order to provide

an insulation layer in addition to the outside electrode part, an alumina paste coated film was used to form an insulation layer coated film.

Separately, a circular cylindrical impedance tube provided with holes with a diameter of 1 mm in the 180° opposite positions was prepared with the same material as that for the green sheet mentioned previously. Next, the previously mentioned coated film rendered green sheet was rolled on this impedance tube so that the electrode to be formed later would cover the holes. By firing, the solid electrolyte proper, the inside electrode, the inside lead drawing part, the outside electrode, the outside lead drawing part, and an insulation layer were obtained. An oxygen sensor element was thus prepared.

Next, on the entire external peripheral surface of this oxygen sensor element, spinel was subjected to melt injection in the same manner as in Application Product No. 5. An oxygen sensor (Comparative Product No. 5) was thus prepared. /5

⑤ Plated comparative product (No. 6)

On the same solid electrolyte proper as that used in the application product, electroless plating was carried out using a tetravalent Pt amine complex salt aqueous solution to form an electrode. An oxygen sensor element was thus prepared.

Next, with respect to this oxygen sensor element, the same heater and alumina insulation layer as in Application Product No. 6 were also provided to prepare the oxygen sensor of Comparative Product No. 6.

With respect to the outside lead drawing part (32B) of the oxygen sensor element related to the comparative product

mentioned previously, the same insulation layer as in the application product was also formed.

(2) Performance tests and performance evaluation

① Initial adherence

The plated film strength on the elements of Application Products Nos. 1 through 4 and Comparative Products Nos. 1 through 4 were evaluated by the tape test.

In the case of Comparative Product No. 1, the adherence of the plating was poor originally. There were those that did not exhibit a sufficient conduction resistance. In the case of Comparative Products Nos. 2 through 4, spalling was large and a low adherence was exhibited.

On the other hand, in the case of Application Products Nos. 1 through 4, no spalling occurred and a high adherence was exhibited.

② Durable adherence

The outside electrode portions (6) of the oxygen sensors of Application Product No. 5 and Comparative Product No. 5 were continuously heated with a Bunsen burner. The temporal change in the adherence between the electrode and the solid electrolyte proper was investigated. The results are shown in Figure 6.

For the oxygen sensor of Comparative Product No. 5, with the continuation of heating, the increase in the sensor's internal resistance was pronounced. However, for the oxygen sensor of Application Product No. 5, even when heating was continued for

1200 h, the increase in the sensor's internal resistance was slight. For a portion of Comparative Product No. 5, spalling occurred between the electrode and the solid electrolyte proper by continuous heating for 500 h.

③ Insulation characteristics of the electrode protective layers

Using the oxygen sensors of Application Product No. 6 and Comparative Product No. 6, the insulation characteristics of the alumina insulation layers were investigated. In other words, using a 50-V-dC insulation resistance instrument at 800°C, the resistance values were measured. The insulation characteristics of the heater buried inside the alumina insulation layer and the outside electrode were evaluated. The results are shown in Figure 7.

For the comparative products, the variation in the insulation resistance was large. Furthermore, those with absolute values of 10 kΩ or so were observed. In comparison to the application products, it showed that the insulation characteristics were decreased. The reason was that plating was not rendered in the portions other than the electrode part due to masking in the plating method for the electrode of Comparative Product No. 6. This was believed to be due to the incomplete masking.

In contrast, the insulation characteristics of the alumina insulation layers in the present application products were sufficiently maintained.

④ Contamination resistance

The oxygen sensors of Application Product No. 5 and Comparative Product No. 5 were installed in the specified exhaust gas pipe, then the tests on the contamination resistance (contamination resistance against lead) of the various elements were carried out. As the durability conditions, the Pb content in gasoline was 50 mg/gal and the bending durability test (a cycle pattern durability test including fully open, medium speed region, and idle) was conducted. The results are shown in Figures 8 and 9. Figure 8 shows the relationship between the elapsed time and response characteristics from the rich exhaust-gas atmosphere (600 mV) to the lean exhaust-gas atmosphere (300 mV). Figure 9 shows the relationship between the control air/fuel ratio and the control frequency of the sensor.

As shown by these, for the oxygen sensor of Comparative Example No. 5, the response characteristics decreased after 1,000 h (Figure 8). With a decrease in the control frequency, the control air/fuel ratio characteristics shifted to a large extent in the rich exhaust-gas atmosphere direction (Figure 9). For the application products, there were essentially no such variations. From these, the comparative products were strongly affected by lead as a contamination substance. This was due to the fact that excessive pores were formed in the electrode part in the formation of the electrode by high-temperature firing, the 3-phase interface of the gas-solid electrolyte-Pt was small, the reactivity with respect to the gas was poor as a result, and the effect of contamination by Pb or the like was strong.

On the other hand, for the oxygen sensor of Application Product No. 5, there were no such problems and it had an extremely good contamination resistance.

(3) Effectiveness of the application examples

According to the method for the manufacture of oxygen sensors related to the present application examples in the manner described previously, an improvement in the adherence strength between the electrode and the solid electrolyte proper, as well as maintenance and improvement of the contamination resistance, insulation characteristics, and other sensor performance levels are possible. Furthermore, since there is a specified platinum concentration, the initial adherence of the electrode is also excellent.

The present invention is not to be restricted to those shown in the specified application examples mentioned previously. Application examples with a variety of changes within the range of the present invention are possible, depending on the objectives and applications.

Effect of the invention

If the oxygen sensor manufacturing method related to the present invention is used, as shown by the effects mentioned previously, an improvement in the adherence strength between the electrode and the solid electrolyte proper, the prevention of spalling of the electrode itself from the solid electrolyte proper during the usage of the oxygen sensor, and so on are possible.

Therefore, by the constitution of the electrode on the noble-metal-nuclei rendered formation part and the plated layer formed on top of it, the adherence with the solid electrolyte proper and the densification characteristics of the plated layers are excellent. Therefore, the contamination resistance, insulation characteristics, and other sensor performances can be maintained and improved.

Brief description of the figures

Figure 1 is a partial cross-sectional diagram showing the state of formation of the inside electrode coated film and the like on the green sheet as the solid electrolyte proper of the oxygen sensor element in an application example. Figure 2 is a partial longitudinal cross-sectional diagram showing the state of formation of a coated film from an organic noble-metal ink on the solid electrolyte proper in an application example. Figure 3 is a partial semilongitudinal cross-sectional diagram of an oxygen sensor related to an application example. Figure 4 is a partial lateral cross-sectional diagram for the explanation of the constitution of the outside electrode and the like in the oxygen sensor related to an application example. Figure 5 is a partial lateral cross-sectional diagram for the explanation of the constitution of the outside electrode and the like of the oxygen sensor with the built-in heater of Application Product No. 6. Figure 6 is a graph showing the temporal change in the sensor's internal resistance. Figure 7 is a graph showing the results of evaluation of the insulation characteristics of the alumina insulation layer by the resistance values. Figure 8 is a graph showing the relationship between the elapsed time and the

response characteristics from a rich exhaust-gas atmosphere to a low exhaust-gas atmosphere. Figure 9 is a graph showing the relationship between the control air/fuel ratio characteristics and the control frequency of the sensor.

1: Green sheet, 1A: Solid electrolyte proper, 2: Inside electrode coated film 2A: Inside electrode, 31: Inside lead drawing part coated film, 32: Outside lead drawing part coated film, 31A: Inside lead drawing part, 32A: Outside lead drawing part, 4: Noble-metal-nuclei rendered formation part coated film, 4A: Noble-metal-nuclei rendered formation part, 5: Plated layer, 6: Electrode, 7: Electrode protective layer, 8: First insulation layer coated film, 8A: First insulation layer, 9: Second insulation layer coated film, 9A: Second insulation layer, 10: Impedance tube, 12: Heater.

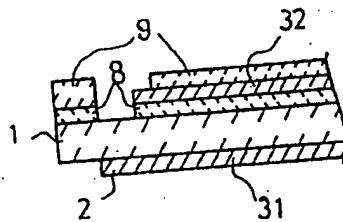


Figure 1

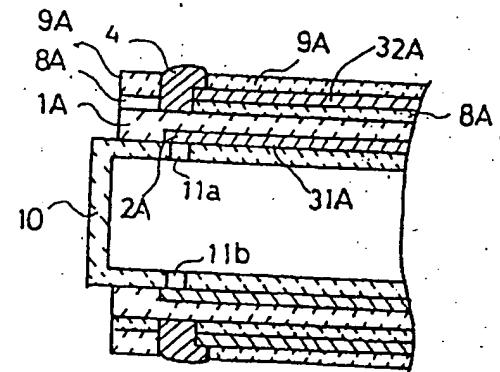


Figure 2

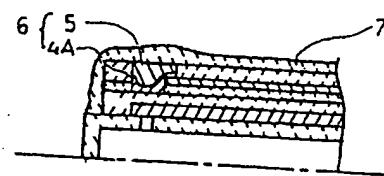


Figure 3

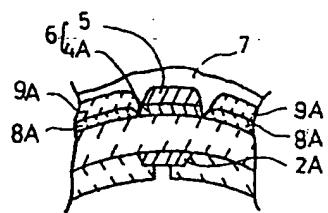


Figure 4

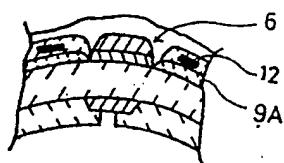


Figure 5

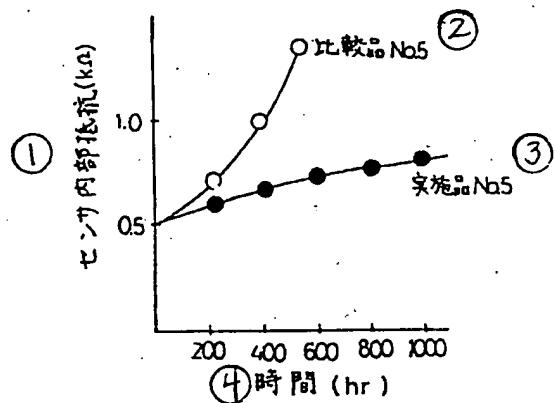


Figure 6

Key: 1 Sensor Internal resistance ($k\Omega$)
 2 Comparative product No. 5
 3 Application product No. 5
 4 Time (h)

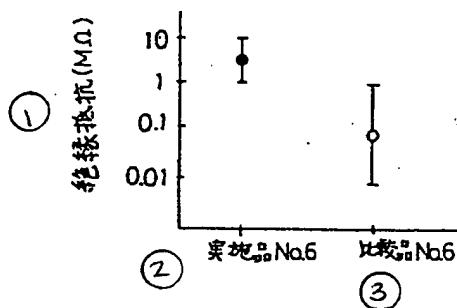


Figure 7

Key: 1 Insulation resistance ($M\Omega$)
 2 Application product No. 6
 3 Comparative product No. 6

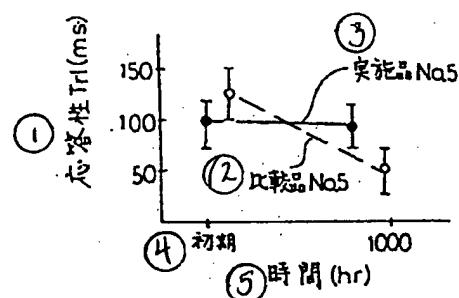


Figure 8

Key: 1 Response characteristics Trl (ms)
 2 Comparative product No. 5
 3 Application product No. 5
 4 Initial time (hr)
 5 Time (h)

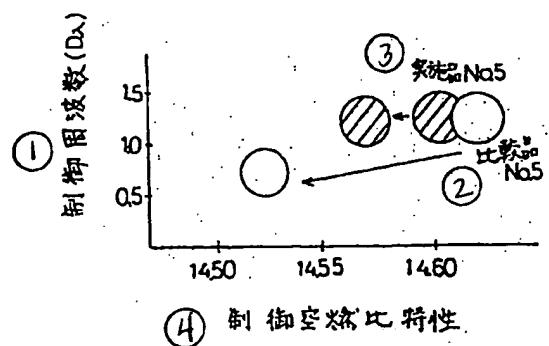


Figure 9

Key: 1 Control frequency ($D\lambda$)
 2 Comparative product No. 5
 3 Application product No. 5
 4 Control air/fuel ratio characteristics